

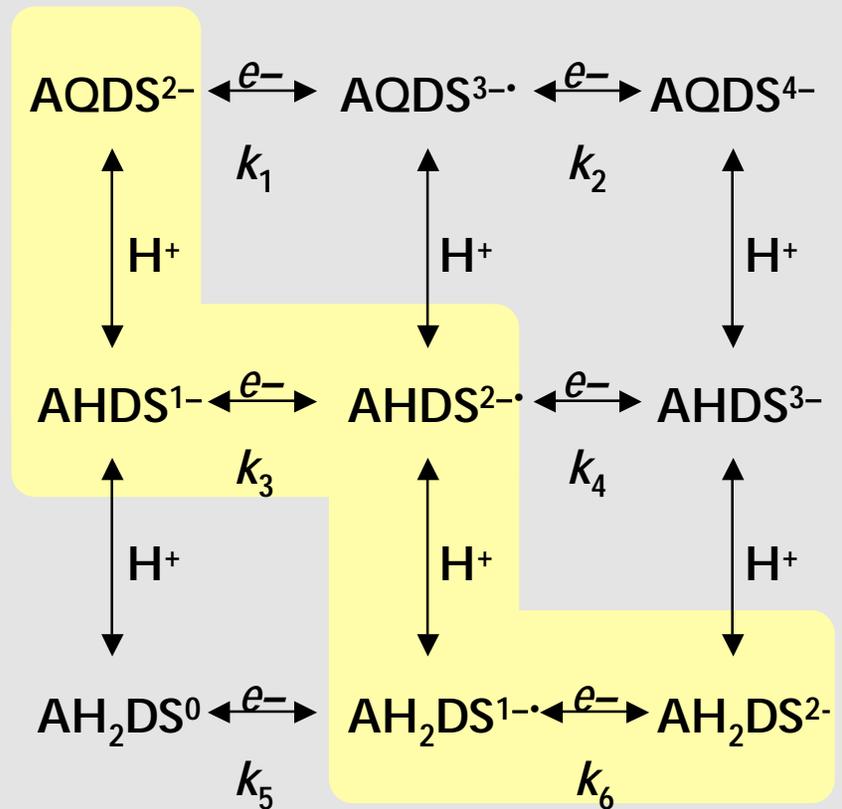
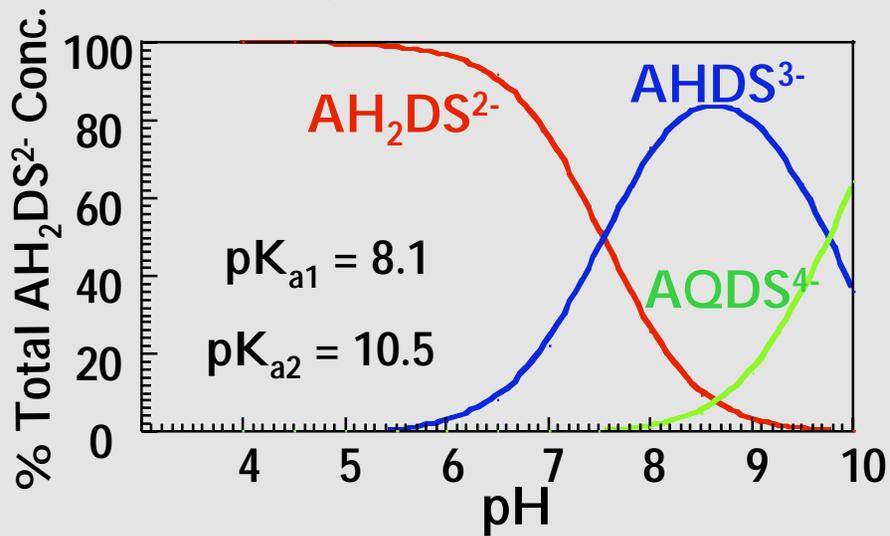
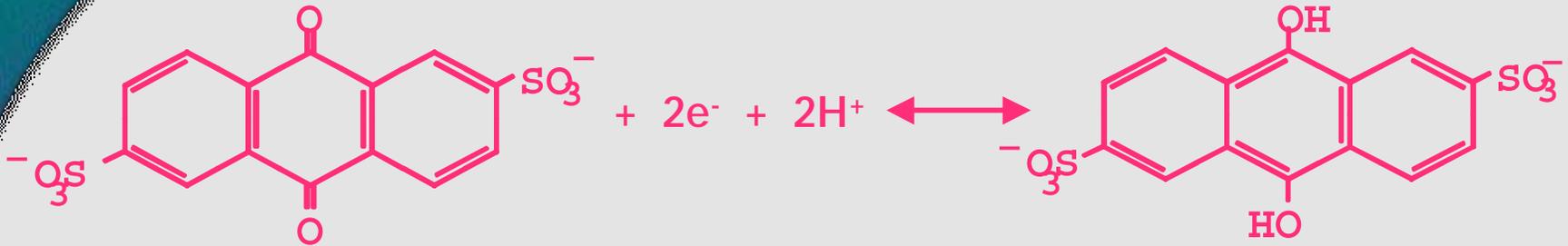
# Reduction of U(VI) Complexes by Anthraquinone Disulfonate: Experiment and Molecular Modeling

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# Rationale

- Past studies demonstrate that complexation will limit abiotic and biotic U(VI) reduction rates and the overall extent of reduction. However, the underlying basis for this behavior is not understood and presently unpredictable across species and ligand structure.
- *The central tenets of these investigations are:*
  - *Reduction of U(VI) follows the electron-transfer (ET) mechanism developed by Marcus;*
  - *The ET rate is the rate-limiting step in U(VI) reduction and is the step that is most affected by complexation;*
  - *Marcus theory can be used to unify the apparently disparate U(VI) reduction rate data and as a computational tool to construct a predictive relationship.*

# AQDS Oxidation/Reduction Reaction Paths



# AQDS Reduction Potentials

Redox Reaction	Calc. E° (V, SHE)	Experimental (V, SHE)
Two electron: AQDS <sup>2-</sup> + 2e <sup>-</sup> + 2H <sup>+</sup> ↔ AH <sub>2</sub> DS <sup>2-</sup>	0.253	0.228; 0.263
AQDS <sup>2-</sup> + 2e <sup>-</sup> ↔ AH <sub>2</sub> DS <sup>4-</sup>	-0.298	-0.323
One electron: AQDS <sup>2-</sup> + e <sup>-</sup> + H <sup>+</sup> ↔ AHDS <sup>2·-</sup>	-0.055	-0.066
AHDS <sup>2·-</sup> + e <sup>-</sup> + H <sup>+</sup> ↔ AH <sub>2</sub> DS <sup>2-</sup>	0.561	0.522
AQDS <sup>2-</sup> + e <sup>-</sup> ↔ AHDS <sup>3·-</sup>	-0.244	-0.255
AHDS <sup>3·-</sup> + e <sup>-</sup> ↔ AQDS <sup>4-</sup>	-0.351	-0.391
AHDS <sup>1-</sup> + e <sup>-</sup> ↔ AHDS <sup>2·-</sup>	-0.012	
AHDS <sup>2·-</sup> + e <sup>-</sup> ↔ AHDS <sup>3-</sup>	-0.085	-0.048
AH <sub>2</sub> DS <sup>0</sup> + e <sup>-</sup> ↔ AH <sub>2</sub> DS <sup>1·-</sup>	0.341	
AQDS <sup>1·-</sup> + e <sup>-</sup> ↔ AH <sub>2</sub> DS <sup>2-</sup>	-0.002	

Rosso et al. 2004. *J. Physical Chemistry A* (in press)

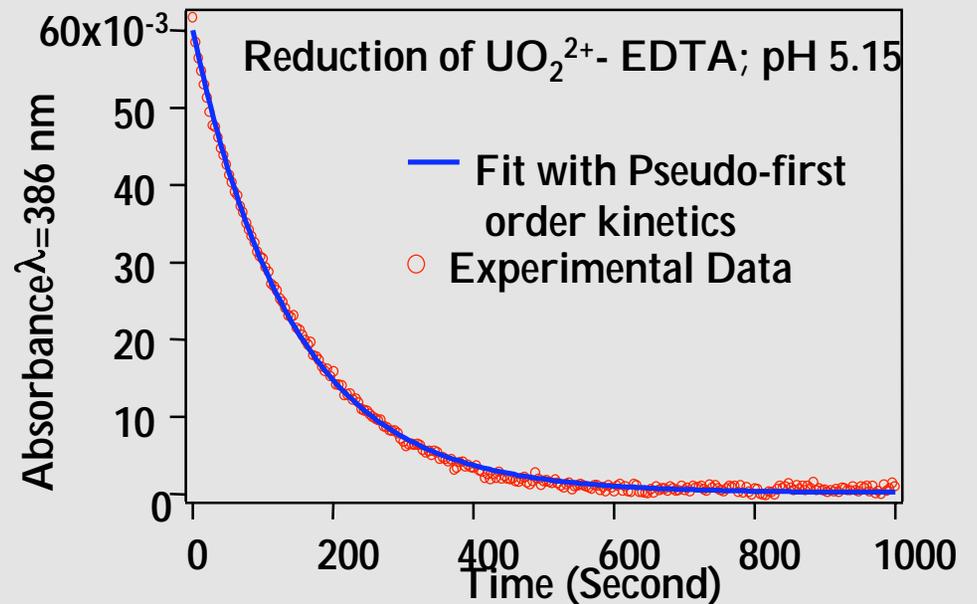
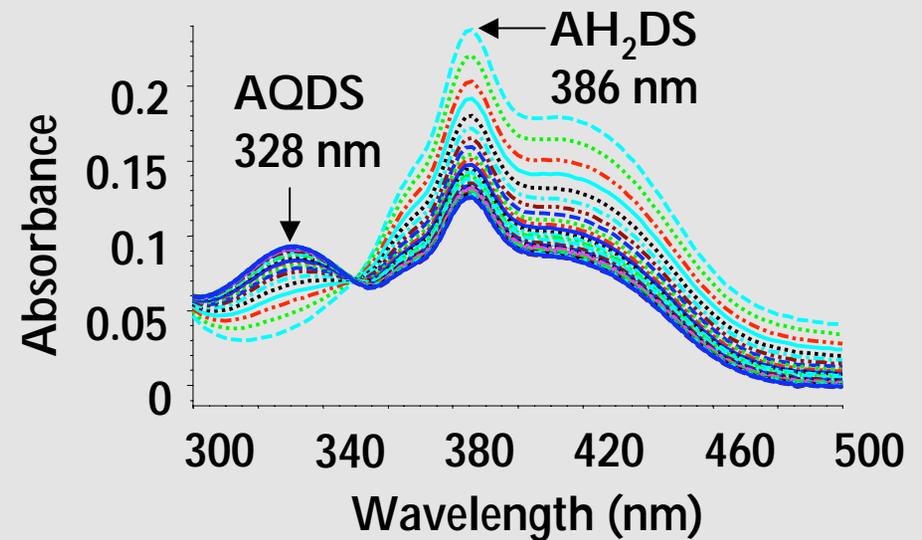
# Experimental Techniques

Diode Array data collection:

- $\lambda$  cut off < 300 nm
- data collection 100 msec to 8 sec
- Total time 30 sec to 3000 sec

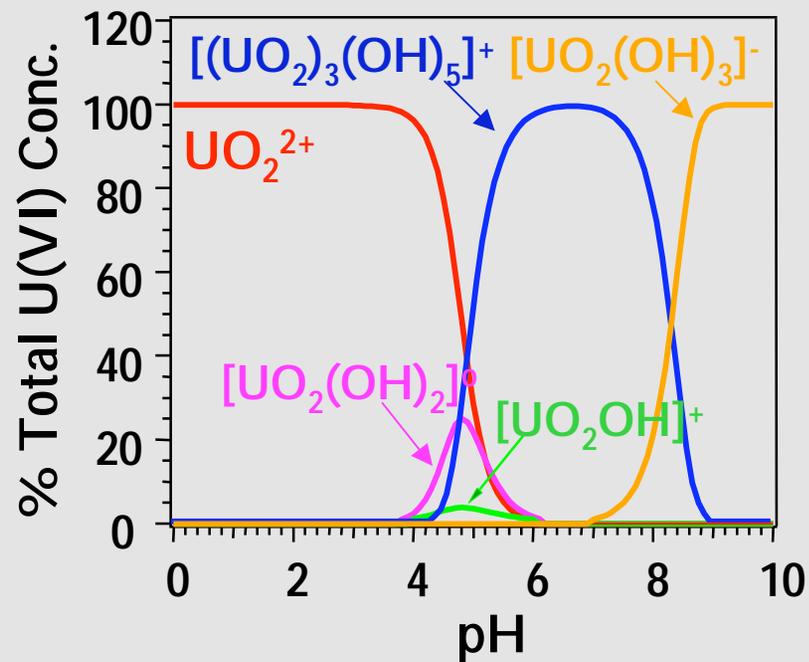
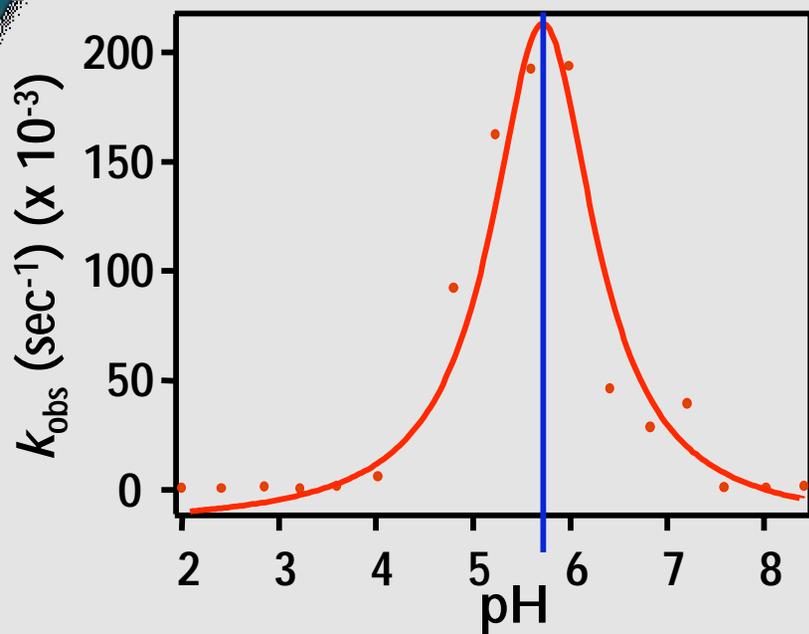


UV/Vis  
Diode  
array



# AH<sub>2</sub>DS Reduction of UO<sub>2</sub><sup>2+</sup> as a Function of pH

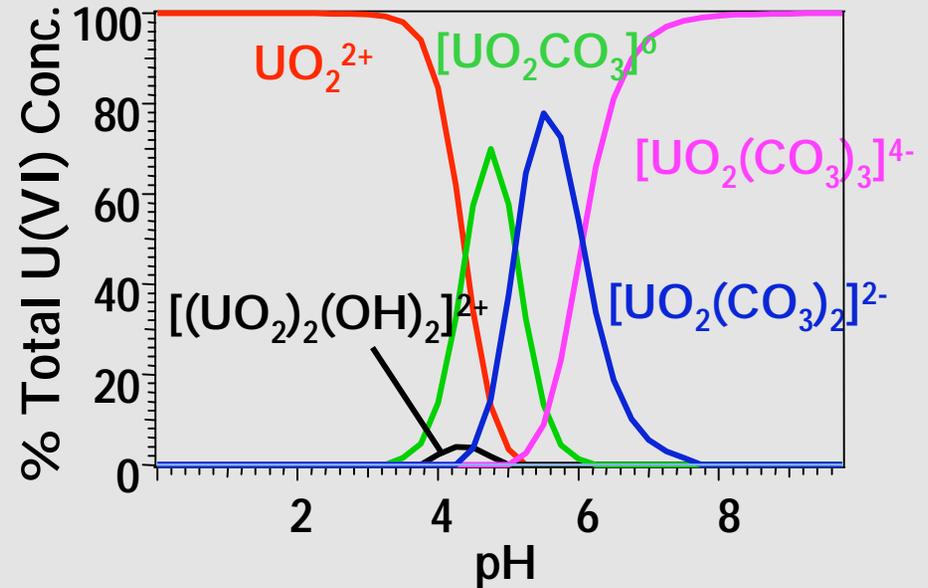
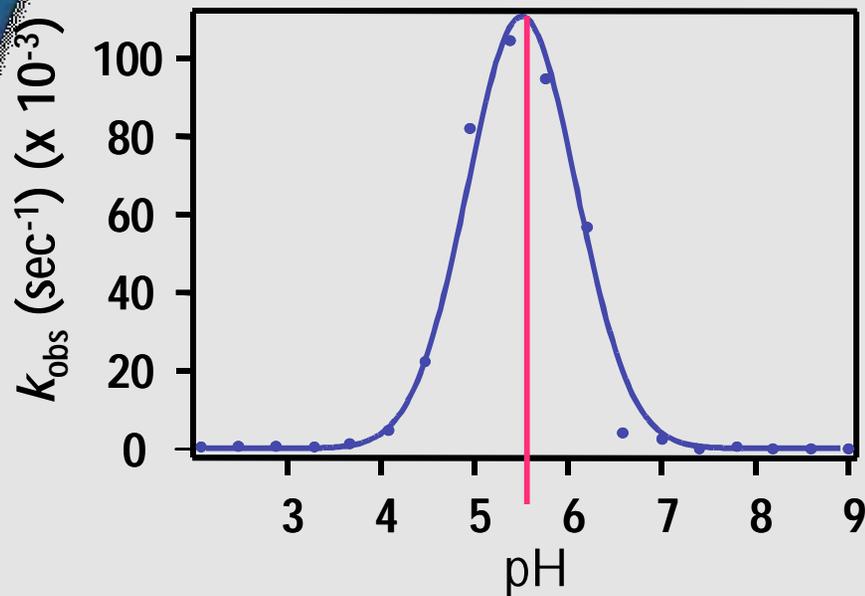
[UO<sub>2</sub><sup>2+</sup>] = 100 μM; [AH<sub>2</sub>DS] = 10 μM; IS = 0.1 M



- ❖  $k_{obs}$  max attained between pH 5.5 and 6.0
- ❖ From its maximum,  $k_{obs}$  decreases by about a factor of 200
- ❖ low pH  $k_{obs}$  – Nernst pH effect which lowers the driving force.
- ❖ pH > 6 – speciation of AH<sub>2</sub>DS and UO<sub>2</sub><sup>2+</sup> hydrolysis

# AH<sub>2</sub>DS Reduction of UO<sub>2</sub><sup>2+</sup> - CO<sub>3</sub> complexes as a Function of pH

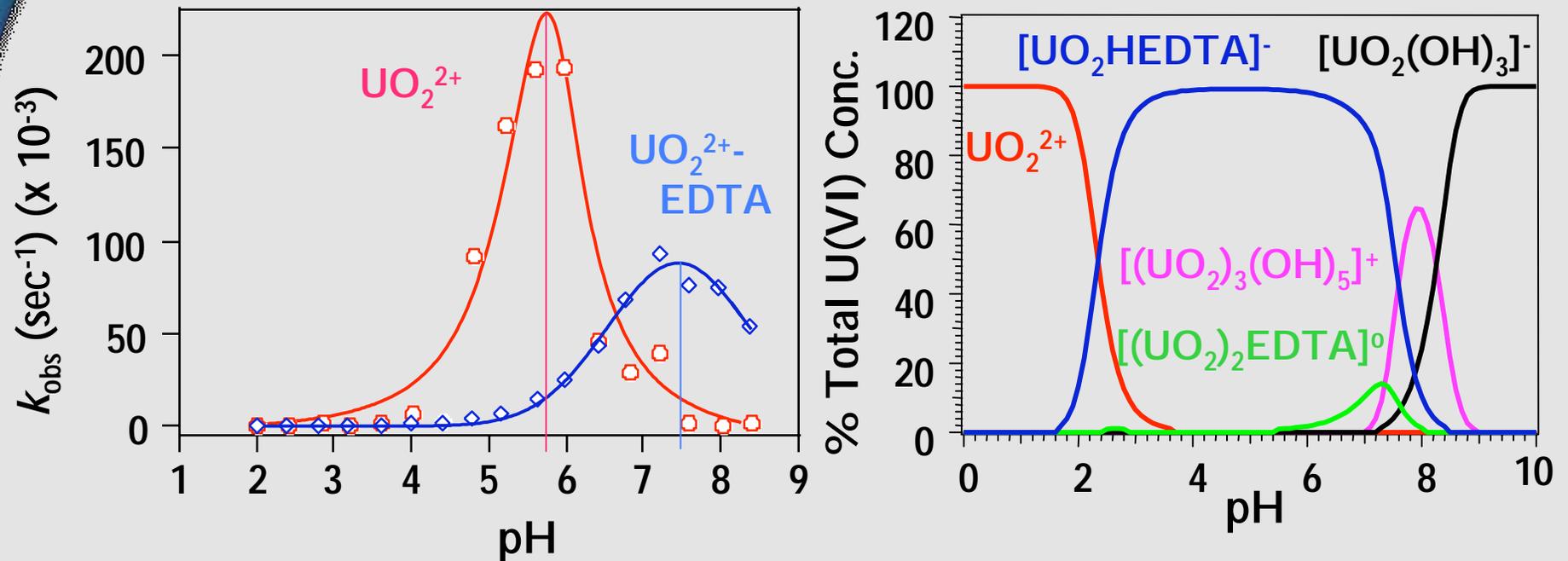
[UO<sub>2</sub><sup>2+</sup>] = 100 μM; [AH<sub>2</sub>DS] = 10 μM; [CO<sub>3</sub><sup>2-</sup>] = 34 mM



- ❖  $k_{obs}$  max attained between pH 5.5 and 6.0
- ❖ From its maximum,  $k_{obs}$  decreases by at least 200x at pH 7.9
- ❖ low pH  $k_{obs}$  – Nernst pH effect which lowers the driving force
- ❖ pH > 6 – speciation of AH<sub>2</sub>DS and UO<sub>2</sub><sup>2+</sup> - CO<sub>3</sub><sup>2-</sup> complexes

# AH<sub>2</sub>DS Reduction of UO<sub>2</sub><sup>2+</sup> - EDTA complex as a Function of pH

[UO<sub>2</sub><sup>2+</sup>] = 100 μM; [AH<sub>2</sub>DS] = 10 μM; [EDTA] = 150 μM

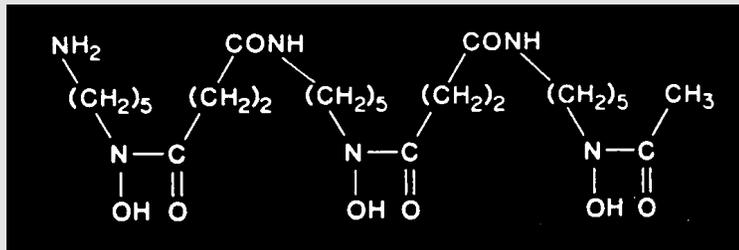


- ❖  $k_{obs}$  max attained at about pH 7.5
- ❖ low pH  $k_{obs}$  – Nernst pH effect and complexation
- ❖ from pH 5.5 to pH 7.5  $k_{obs}$  increases by a factor of only 6.4

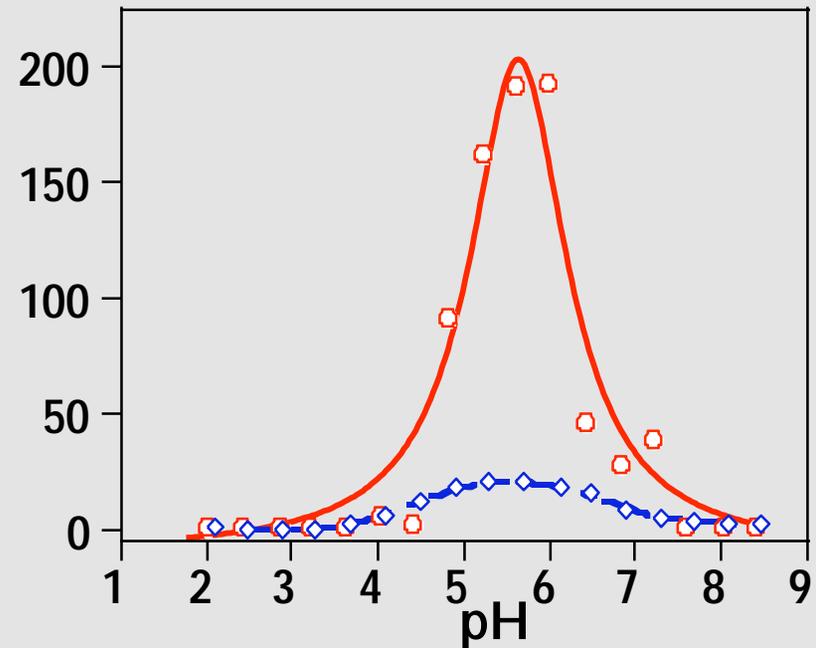
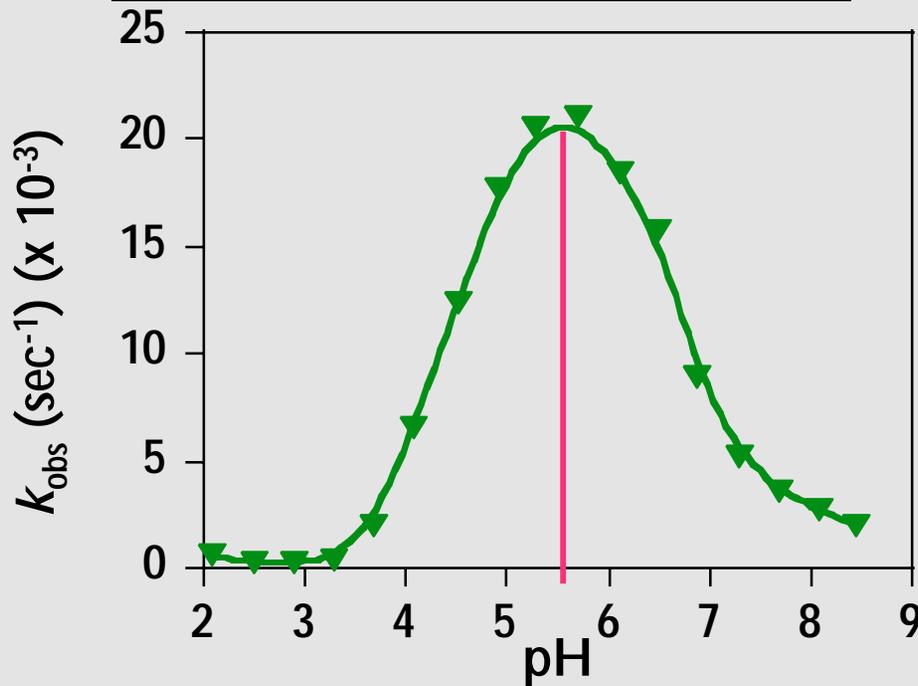
# AH<sub>2</sub>DS Reduction of UO<sub>2</sub><sup>2+</sup> - DFO complex as a Function of pH

[UO<sub>2</sub><sup>2+</sup>] = 100 μM; [AH<sub>2</sub>DS] = 10 μM; [DFO] = 150 μM

## Deferriferrioxamine B (DFO)



Est. log β (UO<sub>2</sub><sup>2+</sup>,L,H) = 10.5 (1,1,1)



# Molecular Modeling - Marcus Theory

- Experimentally observed reactions involve 3 basic steps:
  - o Precursor, or encounter complex, formation ( $K_{pre}$ ) – (charge)
  - o ET within the complex forming the successor complex ( $k^{ET}$ )
  - o Dissociation of the successor complex
- The first  $UO_2^{2+}$  -  $AH_2DS$  ET reaction hypothesized to be rate controlling – second ET fast - within same EC

First-order ET rate constant a function of three primary variables:

$$k^{ET} = \frac{2\pi}{h} H_{AB}^2 \frac{e^{-(\Delta G^{\circ'} + \lambda)^2 / 4RT}}{\sqrt{4\pi RT}}$$

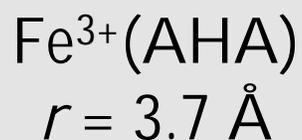
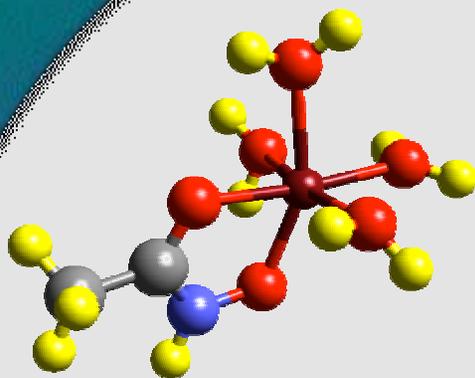
Reorganization energy separable into inner- and outer-sphere terms:

$$\lambda = \lambda_{IS} + \lambda_{OS}$$

Thermodynamic driving force derived from experimental  $\Delta G^{\circ'}$ 's:

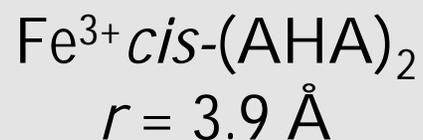
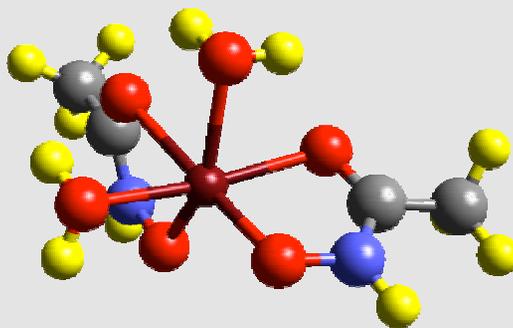
$$\Delta G^{\circ'} = \Delta G^{\circ} - W_R + W_P$$

## Model Results for Fe – AHA Complexes (1:1; 1:2; 1:3)



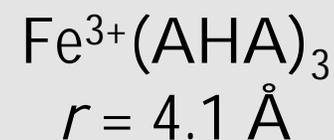
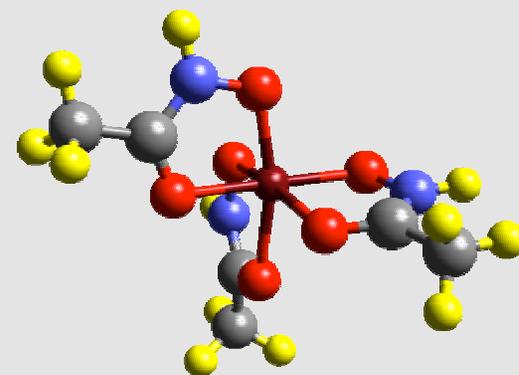
$$\begin{aligned}\lambda_{\text{IS}} &= 1.015 \text{ eV} \\ \lambda_{\text{OS}} &= 1.979 \text{ eV} \\ \lambda_{\text{T}} &= 2.994 \text{ eV}\end{aligned}$$

$$\begin{aligned}\text{exp. } t_{-} &= 0.56 \text{ s} \\ \text{calc. } t_{-} &= 3 \times 10^{-5} \text{ s}\end{aligned}$$



$$\begin{aligned}\lambda_{\text{IS}} &= 1.281 \text{ eV} \\ \lambda_{\text{OS}} &= 2.102 \text{ eV} \\ \lambda_{\text{T}} &= 3.383 \text{ eV}\end{aligned}$$

$$\begin{aligned}\text{exp. } t_{-} &= 0.41 \text{ s} \\ \text{calc. } t_{-} &= 0.55 \text{ s}\end{aligned}$$



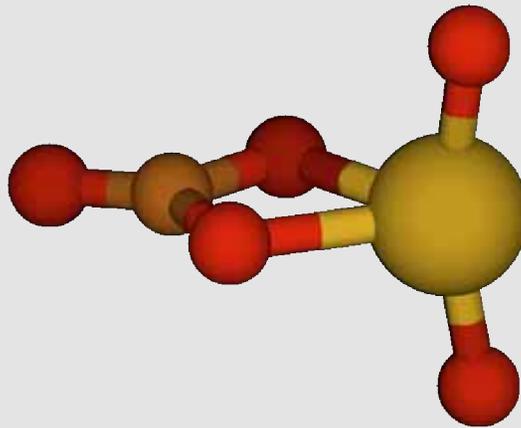
$$\begin{aligned}\lambda_{\text{IS}} &= 0.974 \text{ eV} \\ \lambda_{\text{OS}} &= 2.207 \text{ eV} \\ \lambda_{\text{T}} &= 3.181 \text{ eV}\end{aligned}$$

$$\begin{aligned}\text{exp. } t_{-} &= 5.52 \text{ s} \\ \text{calc. } t_{-} &= 45.4 \text{ s}\end{aligned}$$

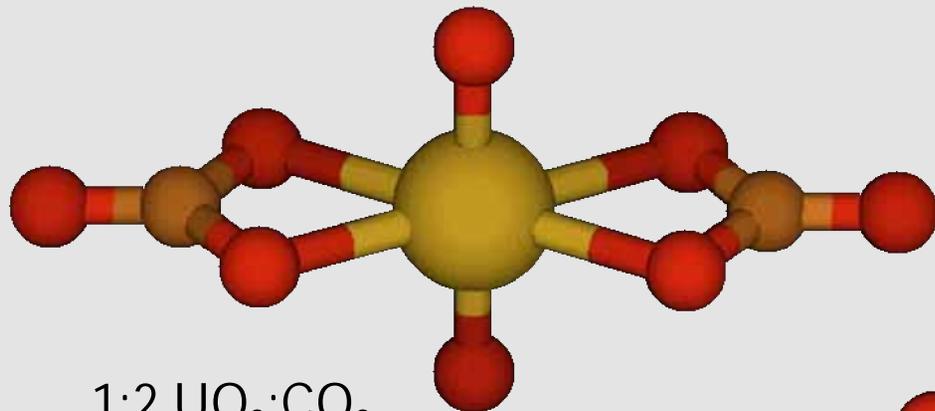
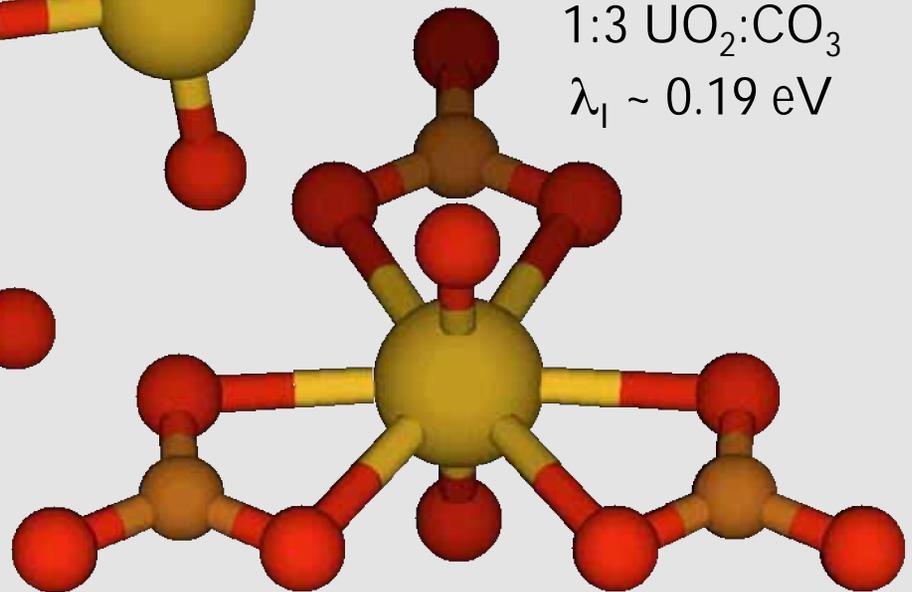
# Modeling of $\text{UO}_2^{2+}$ Species -Carbonate

- $\lambda_1$  is unsystematic for carbonate complexes
- $\lambda_1$  for  $\text{UO}_2^{2+}(\text{OH}_2)_x$  increases systematically from 0.23 eV ( $x = 0$ ) to 0.61 eV ( $x = 6$ )

1:1  $\text{UO}_2:\text{CO}_3$   
 $\lambda_1 \sim 0.97$  eV

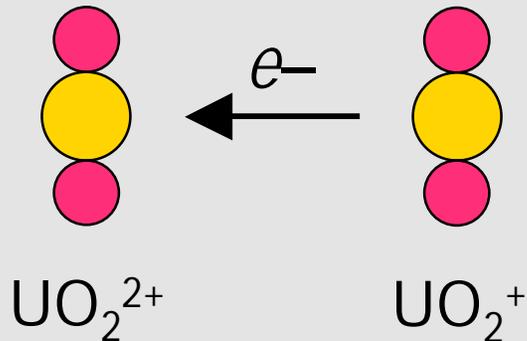


1:3  $\text{UO}_2:\text{CO}_3$   
 $\lambda_1 \sim 0.19$  eV



1:2  $\text{UO}_2:\text{CO}_3$   
 $\lambda_1 \sim 0.01$  eV

# UO<sub>2</sub> Self-Exchange Electron Transfer



Calculated ET rate = 0.3 M<sup>-1</sup> s<sup>-1</sup>  
Experimental = 1 – 15 M<sup>-1</sup> s<sup>-1</sup>

Ref. Howes et al. (1988)

Conditions:

aqueous solution  
zero ionic strength  
room temperature

UO<sub>2</sub><sup>2+</sup> Reduction by AH<sub>2</sub>DS

Calculated log ET (M<sup>-1</sup> s<sup>-1</sup>)



4.0



-6.4

# Conclusions

- Under the studied pH conditions, homogeneous aqueous phase  $\text{UO}_2^{2+}$  species are reduced by  $\text{AH}_2\text{DS}$ .
  - At low pH ( $< 4$ )  $k_{obs}$  is dominated by a Nernst pH effect that decreases the driving force ( $\Delta G^\circ$ ) and reduces the reaction rate
  - Reduction rate is dependent on stoichiometry, structure, and nature of the ligand.
- The observed reduction rate behavior for  $\text{UO}_2^{2+}$  complexes is semi-quantitatively consistent with expectations from Marcus theory.
  - Larger ligands tend to slow the rate by increasing the ET distance, decreasing the electronic coupling, and increasing the ET barrier.
  - Higher ligand numbers tend to slow the rate by creating more negatively charged complexes and lower reduction potentials.

# Future Studies

## Experimental:

- Variable reactant concentrations at  $\text{pH} = \text{max. } k_{obs}$
- Investigate conformational shielding of the U(VI) cation by the polyelectrolytes (i.e., polyacrylic acid and polymaleic acid).
- Investigate  $\text{UO}_2^{2+}$  species reduction rates in the presence of hematin.

## Modeling:

- Verify our hypothesis that two electrons are transferred sequentially within a single EC, and that the 1<sup>st</sup> ET is rate limiting.
- Ultimately, construct  $\text{pH vs } k_{obs}$  curves that are experimentally observed.